

-14-
CLAIMS

1. A process for producing a surface-modified layer system comprising a substrate having a surface and a self-assembled monolayer (SAM) anchored to at least part of said surface, wherein said SAM is comprised by aryl or rigid alicyclic moiety species, said process comprising the steps of:
 - a) providing a SAM anchored to a substrate, wherein said SAM is polymorphic having at least first and second structural forms; and
 - b) thermally treating said SAM so as to change said SAM from said first structural form to said second structural form.
2. A process according to claim 1, which process includes the preliminary steps of:
 - a) providing a said substrate and a compound having a selected said aryl or rigid alicyclic moiety species and an anchor moiety bondable to said substrate so as to exert a directive force with respect to the molecular orientation of said compound, said selected aryl moiety species having a plurality of different parameters affecting the energy-balance of the SAM, wherein at least two of said parameters exert opposing directive forces arising from the molecule-substrate interaction which have a substantially competitive effect on said energy-balance which results in polymorphism of said SAM; and
 - b) bonding of said compound to said substrate.
3. A thermo-lithographic process comprising a process according to claim 1 or claim 2 wherein a desired pattern is transferred to said SAM using said thermal treatment so as to change selectively part of said SAM from said first structural form to said second structural form.

-15-

4. A process according to claim 3 wherein in said pattern transferring step there is used a thermal treatment applied selectively to only part of the SAM in accordance with a negative image of said desired pattern so that the thermally treated areas are rendered more stable compared to the untreated ones.
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5. A process according to claim 3 or claim 4 wherein said thermal treatment is selected from: direct contact with a heated body or a heated fluid; and exposure to thermal radiation.
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6. A process according to claim 5 wherein said radiation is pulsed.
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7. A process according to any one of claims 3 to 6 wherein said SAM is raised to a temperature of at least 100°C.
8. A process according to any one of claims 3 to 7 wherein the thermal treatment is carried out in a substantially inert environment.
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9. A process according to any one of claims 3 to 8 wherein said thermal treatment is formed and arranged for parallel-form pattern transfer.
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10. A process according to any one of claims 3 to 8 wherein said thermal treatment is formed and arranged for serial-form pattern transfer.
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11. A process according to any one of claims 3 to 10, which process includes the further step of developing the thermally treated SAM by subjecting it to further processing so as to substantially modify selectively one

-16-

of: thermally treated and non-thermally treated parts of the SAM.

12. A surface-modified layer system comprising a substrate having a surface and a self-assembled monolayer (SAM) anchored to at least part of said surface, wherein said SAM is comprised by a aryl or rigid alicyclic moiety species in a substantially stable structural form derived, *in situ*, by thermal treatment from a less stable structural form.
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13. A system according to claim 12 wherein said substrate comprises a conductor or semiconductor material.
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14. A system according to claim 12 or claim 13 wherein said material comprises at least one of gold, silver, chromium, manganese, vanadium, tungsten, molybdenum, zirconium, titanium, platinum, aluminium, iron, steel, indiumphosphide, gallium arsenide, and alloys and oxides thereof, including glasses.
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15. A system according to any one of claims 12 to 14 wherein said SAM is comprised by a compound which comprises an anchor moiety, and an optionally substituted, aryl (including hetero-aryl) moiety.
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16. A system according to claim 15 which includes a spacer moiety between the anchor moiety and the aryl moiety.
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17. A system according to claim 15 or claim 16 wherein said anchor moiety is selected from thio, seleno, carboxyl, phosphonate, phosphate and hydroxyl.
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18. A system according to any one of claims 12 to 17 wherein said aryl or rigid alicyclic moiety is selected from phenyl, biphenyl and terphenyl, and fused ring systems
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-17-

selected from anthracyl and naphthyl, and hetero-aryl selected from bipyridyl, terpyridyl, thiophenyl, bithienyl, terthienyl and pyrrolyl and alicyclic moieties selected from bridged alicyclic systems such as bi-, tri-, or tetracycloalkanes.

19. A system according to claim 18 wherein said aryl moiety has at least one substituent selected from halogen, carboxy, trifluoromethyl, thiol, hydroxy, cyano, amino, nitro, C1 to C6 alkyl, and carbonyl.
20. A system according to claim 16 or any of claims 17 to 19 when dependent on claim 16, wherein said spacer group is selected from C1 to C12, saturated or unsaturated hydrocarbon, other structures containing at least one of an ether linkage, and an amide group, and up to C12 cycloalkyl.
21. A system according to any one of claims 12 to 20 wherein said substrate comprises gold, said anchor moiety comprises thiol, and the hydrocarbon spacer group is selected from C2, C4, C6, C8, and C10, alkyl.
22. A system according to any one of claims 12 to 20 wherein said substrate comprises silver, said anchor moiety comprises thiol, and the hydrocarbon spacer group is selected from C1, C3, C5, C7, and C9, alkyl.
23. A system according to any one of claims 12 to 22 wherein said SAM is a 4-(4'-Methyl-biphenyl-4-yl)-alkane-1-thiol.
24. A system according to claim 23 wherein said alkane is C1 to C10 alkane.